INVESTIGATION OF ALBERTA OIL SAND ASPHALTENES
USING THERMAL DEGRADATION REACTIONS

T. Ignasiak, T.C.S. Ruo and O.P. Strausz

Hydrocarbon Research Centre
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada T6G 2G2

INTRODUCTION

Thermal breakdown reactions directed toward cracking complex molecules into low molecular weight products constitute an important part of oil sand technologies (1). It is generally accepted that the high asphaltene content of Alberta bitumen is primarily responsible for a large proportion of the coke produced by dehydrogenation and repolymerization reactions that prevail at high temperatures. Moreover, asphaltene obtained from the Alberta oil sands contains appreciable amounts of heteratoms, mainly sulfur, oxygen and nitrogen, that tend to be associated with coke precursors and as such greatly reduce the marketable value of coke as an energy source. However, our previous results (2-6) suggest that the oxygen-based hydrogen bonding and sulfide linkages play important roles in the molecular size of the sulfur-rich Alberta oil sand asphaltene. These observations are significant because the energy requirement for the cleavage of sulfide bonds is generally lower than that required for coke formation. We have therefore undertaken a study of the thermal behaviour of asphaltene under moderate conditions aimed at high product recoveries and low coke yields.

EXPERIMENTAL

The origin of the samples and the preparation of asphaltenes have been described (2,3).

Thermal degradation

The pyrolysis of asphaltene (1.5 g) was carried out in a vacuum (0.1 torr) sealed tube (vol. 40 ml) inserted in a furnace maintained at a preset temperature. After the heating period the tube was cooled to -15°C, opened, and the product Soxhlet extracted with n-pentane to yield the pentane-soluble (maltene) fraction. Subsequent extraction with benzene yielded the benzene soluble (retrieved asphaltene) fraction.

Reduction

A one gram sample of asphaltene dissolved in 15 ml dry THF was introduced to 100 ml liquid ammonia, followed by 45 ml of 98% ethanol and then lithium metal (6 g) cut into small pieces was gradually added over a period of about 1 hour. The mixture was stirred for another 2 hours and finally quenched with 15 ml ethanol. Ammonia was allowed to evaporate overnight. The reduced product was recovered by the usual procedure involving acidification with aqueous HCl, filtration, removal of inorganic salts by water extraction, and was then dried in $vacuo$ at 60°C for 24 hours.

Chromatography separation of pentane soluble fractions

A compound class separation was performed on a glass column, 100 cm x 1 cm (i.d.) packed with silica gel Woelm (activated overnight at 140°C). The sample to solvent ratio was 1:65 (for elution solvents, see Table 5). To assure purity of the fractions, they were monitored by HPLC on a μ-Porasil column using a UV detector.

A clear-cut separation of saturates from olefins was achieved by semipreparative HPLC on a silver aluminum silicate column (column, 6 cm x 0.9 cm (i.d.); solvent, heptane; flow rate, 9 ml/min; pressures, ~8~900 psi).

The molecular weights were determined by vapor pressure osmometry at a nominal concentration of 20 mg/ml in benzene.

RESULTS AND DISCUSSION

1. Thermal degradation of asphaltene

Athabasca asphaltene was heated either at constant temperature for various periods of time or at different temperatures for constant time periods (Table 1).

The yield of the pentane-soluble (maltene) fraction does not seem to increase significantly either during prolonged heating or with increasing temperature but high temperature leads to coke formation. Volatiles and coke are produced at the expense of residual asphaltene.

The elemental analyses of maltene, residual asphaltene and insoluble residue, if any, are given in Table 2. The chemical composition of the maltene fraction does not show much variation with either time of heating or temperature; it is more saturated than the residual asphaltene and distinctly lower in nitrogen content than both the original and residual asphaltenes. In the residual asphaltene, the lower H/C ratios indicate that aromatization increases with either reaction time or increased temperature. The insoluble residue produced at 390°C is the most unsaturated portion of pyrolyzed asphaltene and contains the highest concentration of heteroatoms. Under the conditions used, the overall desulfurization does not exceed 22% in terms of the sulfur present in the parent asphaltene.

In earlier studies (3,6) it was found that the amount of sulfur in bridges susceptible to cleavage in potassium-THF solution varies for Athabasca, Cold Lake, Peace River and Lloydminster asphaltenes. To estimate to what extent these structural variations in the Alberta oil sand asphaltenes are reflected in their thermal behaviour, these asphaltenes were heated under conditions where thermolysis of the Athabasca asphaltene gives optimal conversion and no coke.

At 300°C, after 72 hours, (Table 3), all these sulfur-rich asphaltenes retain full solubility in benzene. Some variations are, however, indicated by the yield of pentane solubles which is the highest for Athabasca and significantly lower for the remaining asphaltenes. This roughly corresponds to the decrease in the molecular weight of the heated asphaltenes. Desulfurization accounts for up to 15% of the original sulfur content and deoxygenation varies from 20 to 40%.

2. Thermal degradation of reduced asphaltene

According to the previous results, (2,7) depolymerization of asphaltene depends to a large extent on the cleavage of C-S bonds and thermolysis at 300°C will involve only the most unstable ones. Any structural changes in the asphaltene molecule which would lower the energy of activation for cleavage of the C-S bonds present may enhance the degradation under the same conditions. It was therefore of interest to investigate the thermal behaviour of asphaltene that had been chemically modified by reduction with alkali metals. The reductive systems applied were potassium in tetrahydrofuran with naphthalene as a charge transfer catalyst (2) and lithium in liquid ammonia in the presence of ethanol. In both cases simple protonation results in partial insolubilization which accounts for up to 60% of reduced asphaltene.

a) Potassium-THF-naphthalene reduced Alberta sulfur-rich asphaltenes

When heated at 300°C for 72 hours these reduced and protonated asphaltenes (Table 4) exhibit thermal properties which are distinctly different from those of naturally occurring asphaltenes, cf. Table 3. Thus thermally treated reduced asphaltenes became almost fully soluble in benzene; the yield of pentane solubles was doubled (except for the case of the Athabasca sample) and the loss of sulfur upon conversion was also twice that observed for unreduced asphaltenes, cf. Table 3. The overall desulfurization upon reduction and thermolysis, about 50%, is comparable for all four asphaltenes.

179

b) Lithium-liquid ammonia reduced Athabasca asphaltene

The treatment with lithium in liquid ammonia in the presence of ethanol en-hances the thermal reactivity of Athabasca asphaltene to an even larger extent than that with potassium in THF. The rate of conversion into pentane solubles and desul-furization have been found to be directly related to the amount of hydrogen intro-duced to asphaltene on reduction. This again seems to depend on the lithium and ethanol concentrations. The enhanced degree of hydrogenation of asphaltene in the presence of ethanol is apparently due to the fact that ethanol as a proton source is more acidic than ammonia and facilitates the reduction of aromatic systems such as benzene derivatives having high negative reduction potentials.

The results (Table 4) show that at 300°C lithium reduced Athabasca asphaltene yielded close to 50% of pentane solubles, and the sulfur content was depleted by about 50%. It is interesting to note that the proportion of hydrogen to carbon in the reduced and heated asphaltene is more favorable than in the original asphaltene. The conversion rate is distinctly higher than in the case of potassium-THF pretreat-ment and comparable with that obtained in the case of the tetralin reaction at 390°C (7).

It is apparent that the high thermal reactivity of reduced asphaltenes as com-pared to the original asphaltene and reflected by appreciable conversion and desul-furization, is related to the cleavage of carbon-sulfur bonds and to partial satura-tion of double bonds. This leads to the formation of thermally unstable thiols which are easily removed at temperatures as low as 300°C.

3. Characterization of the pentane-soluble fraction obtained from thermal degradation of Athabasca asphaltene

The appreciable yields and relatively low molecular weights of the pentane soluble fractions obtained from thermal treatments of asphaltene make them amenable to chromatographic separation. The pentane-soluble products of Athabasca asphaltene, pyrolyzed neat at 300° and 390°C, and in the presence of tetralin at 390°C, and of lithium reduced and pyrolyzed asphaltene at 300°C, have been separated into compound classes on silica gel. The results (Table 5) indicate that the yields of saturates and aromatics increase with increasing temperature of thermolysis at the expense of the polar I and polar II fractions. Significantly, pretreatment with lithium in liquid ammonia in the presence of ethanol promotes the formation of saturates and aromatics I, the yields of which, at 300°C, approximate those obtained at 390°C.

CONCLUSIONS

It is clear from the data presented here that the early stage of low tempera-ture degradation is a gradual depolymerization, where the crosslinking bonds in the asphaltene molecule are preferentially broken with the formation of lower molecular weight, pentane-soluble polar materials. Polar fractions can readily undergo therm-olysis to generate hydrocarbons (e.g., saturates and aromatics).

The alkali metal pretreatment activates certain C-S bonds, most likely by gen-eration of thiols which can be easily removed, thus affording an appreciable overall desulfurization on subsequent pyrolysis. The reduction using lithium/liquid ammonia in the presence of ethanol represents a situation in which the hydrogen added to as-phaltene molecule reacts with the free radicals produced during thermolysis, thus stabilizing the fragments and resulting in a remarkable conversion into pentane-soluble materials.

ACKNOWLEDGMENTS

REFERENCES

(1) Watson, W.T., Energ. Processing, Canada, 62 (1974).
(2) Ignasiak, T., Kemp-Jones, A.V. and Strausz, O.P., J. Org., 42, 312 (1977).
(3) Ignasiak, T., Kemp-Jones, A.V. and Strausz, O.P., Preprints, Div. Fuel Chem.,
     ACS, Symposium on Oil Sand and Oil Shale, 2nd Annual Joint Meeting, Chemical
     Institute ofCanada/American Chemical Society, Montreal, Canada, May 29-June 2,
     1977, Vol. 22, No. 3, pp.126-131.
(4) Kemp-Jones, A.V. and Strausz, O.P., Preprints, Div. Fuel Chem., ACS, Symposium
     on Oil Sand and Oil Shale, 2nd Annual Joint Meeting, Chemical Institute of
     Canada/American Chemical Society, Montreal, Canada, May 29-June 2, 1977, Vol.
     22, No. 3, pp.132-139.
(5) Ignasiak, T., Strausz, O.P. and Montgomery, D.S., Fuel, 56, 359 (1977).
(6) Kemp-Jones, A.V., Ignasiak, T. and Strausz, O.P., in "Oil Sand and Oil Shale
     Chemistry", O.P. Strausz and E.M. Lown, Eds., Verlag Chemie International,
     1978, p.211.
(7) Ignasiak, T. and Strausz, O.P., Fuel, in press.

Table 1. Thermolysis of Athabasca Asphaltene

Temp., °C	Time, hrs	Volatiles	Soluble fraction		Residue	Desulfurization %
			Pentane	Benzene		
300	4	0	20	80	0	9
300	30	1	22	77	0	9
300	72	5	28	67	0	14
300	114	5	26	69	0	14
348	4	4	24	72	0	14
390	4	10	32	38	20	22

Table 2. Elemental analyses of maltene and residual asphaltene
obtained from thermolysis of Athabasca asphaltene

Temp., °C	Time, hrs	MW	H/C	N	O	S
Maltene fraction						
300	4	690	1.36	0.60	2.02	7.00
300	30	680	1.38	0.51	1.59	6.75
300	72	530	1.38	0.55	1.23	6.39
300	114	570	1.40	0.65	1.30	6.40
348	4	620	1.40	0.51	1.60	6.58
390	4	430	1.42	0.50	1.16	6.10
Residual asphaltene						
300	4	6100	1.18	1.29	1.90	7.00
300	30	5500	1.16	1.33	1.84	7.20
300	72	6600	1.07	1.37	1.80	7.21
300	114	4500	1.04	1.34	1.90	7.15
348	4	5300	1.11	1.34	2.00	7.05
390	4	2400	1.06	1.40	1.80	6.88
Residue						
390	4	-	0.89	1.63	2.16	7.16

The % header spans N, O, S columns.

Table 3. Thermolysis of Alberta asphaltenes at 300°C/72 hrs.

Asphaltene		Product			
Source	MW	Conversion Wt %	Loss, Wt %		MW
			Sulfur	Oxygen	
Athabasca	6000	28	14	40	1300
Cold Lake	8100	7	5	30	5500
Peace River	9500	14	14	40	2500
Lloydminster	9300	14	15	20	3500

Table 4 - See following page.

Table 5. Chromatographic separation of the pentane soluble products
from thermally treated Athabasca asphaltene

Eluate	Fraction	Yield, wt % (pentane solubles = 100%)			
		390°C		390°C	
		neat	tetralin	neat	Lithium reduced
$n\text{-}C_5$	Saturates	12.1	15.1	3.2	11.3
	Olefins	2.7	1.9	0.8	1.3
$n\text{-}C_5$/15% Bz	Aromatic I (mono-, di-)	13.7	13.2	5.8	10.9
$n\text{-}C_5$/15% Bz	Aromatic II (> di-to poly-)	30.6	27.5	17.8	19.9
100% Bz	Polar I	22.5	26.3	47.3	30.9
THF	Polar II	15.5	18.4	29.9	24.6

Table 4. Thermolysis of reduced asphaltenes at 300°C/72 hrs.

Asphaltene	Volatiles by weight loss wt %	Solubility in benzene wt %	H/C ratio	MW	Conversion (pentane solubility) wt %	Sulfur content (wt %)			Overall Desulfurization %
						Original	Reduced	Reduced and Heated	
K/THF/Nap reduction									
Athabasca	6	94	1.19	1300	32	8.00	5.75	4.05	49
Cold Lake	5	95	1.19	2500	18	7.97	5.22	4.21	47
Peace River	7	93	1.22	1500	28	8.75	6.11	4.25	51
Lloydminster	7	93	1.19	1500	25	8.30	5.20	3.87	53
Li/NH$_3$/Eth reduction[a]									
Athabasca	9	91	1.35	1000	48	8.00	6.48	3.91	51

[a] H/C of reduced asphaltene = 1.48.